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(54) Hydrocarbon fuel compositions incorporating nitrogen-containing dispersants.

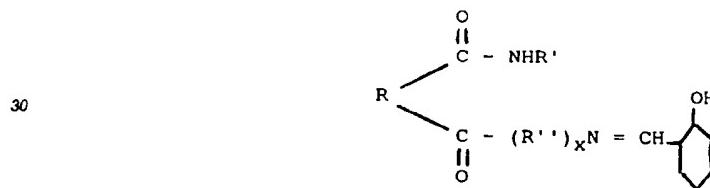
(57) A hydrocarbon fuel composition comprising a hydrocarbon fuel and an amount sufficient to provide dispersancy of a hydrocarbyl-substituted succinic diamide, wherein the hydrocarbyl substituent, which is advantageously a polyisobutene, is of a size sufficient to render the diamide soluble in the fuel, typically from 35 to 300 carbon atoms, and the diamide is obtained by reacting at elevated temperature a secondary amine, for example an N-alkyl piperazine, with either a hydrocarbyl-substituted succinic acid or an anhydride, ester or monoamide derivative thereof.

The present invention relates in general to internal combustion engine fuel compositions. In particular the invention relates to the use of nitrogen-containing compounds as dispersants in the aforesaid fuel compositions.

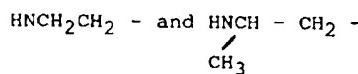
5 The use of nitrogen-containing compounds for the purpose of maintaining sludge-forming deposits dispersed in internal combustion engine lubricating oils, thereby keeping the piston and piston rings relatively free of deposits, is well known. Nitrogen-containing compounds which have long been used as dispersant/detergent additives in lubricating oils include the hydrocarbyl-substituted succinimides. The preparation of succinimides and their use as lubricating oil additives is described in, for example, US-A-3,024,237; US-A-3,202,678; US-A-3,219,666 and US-A-3,275,554.

10 Hydrocarbon fuels generally contain numerous deposit-forming substances. When used in internal combustion engines, deposits tend to form on and around constricted areas of the engine in contact with the fuel. In diesel engines, deposits tend to accumulate in the fuel injection system, thereby hampering good performance of the engine. In automobile engines deposits can build up on engine intake valves leading to progressive restriction of gaseous fuel mixture flow into the combustion chamber and also to valve sticking. It is common practice to incorporate a detergent in the fuel composition for the purpose of inhibiting the formation, and facilitating the removal, of engine deposits, thereby improving engine performance. Nitrogen-containing compounds commonly used as additives in hydrocarbon fuels include polyisobutene amines. Their use is described in, for example, US-A-3,565,804; US-A-3,756,793; and US-A-4,877,416. Polyisobutene succinimides have also been disclosed as hydrocarbon fuel additives in, for example, EP-A-0147240.

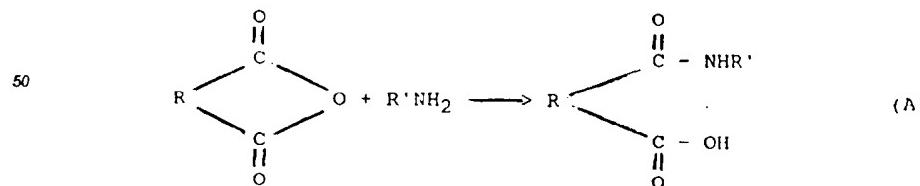
15 20 Although there are references in the prior art to the use of polyisobutene succinic amide-containing materials as additives to fuel compositions, there would not appear to be any specific mention in this context of the use of hydrocarbyl-substituted succinic diamides obtainable by reacting at elevated temperature a hydrocarbyl-substituted succinic acid or an anhydride, ester or monoamide derivative thereof with a secondary amine. Thus, US-A-3,236,613 discloses petroleum distillate hydrocarbon fuels containing from between about 25 1 to about 100 pounds, per thousand barrels of fuel, of a compound of the following formula:



35 40 wherein R is the aliphatic residue of an aliphatic dicarboxylic acid, R' is an aliphatic hydrocarbon group, R'' is a member from the group consisting of



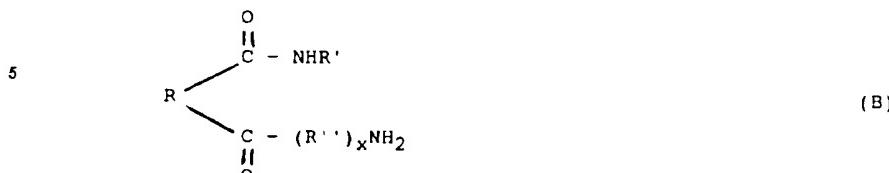
45 and x is an integer from 1 to 6. Such compounds can be prepared by heating at 75 to 100°C for about 2 hours a mole to mole mixture of an aliphatic dicarboxylic acid anhydride and aliphatic primary amine to form the amic acid, ie



55 subjecting the amic acid (A) to condensation reaction at 95°C to 150°C for 2 to 5 hours with a polyamine of the following formula:



in substantially molar amounts to provide the following condensation reaction product:



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and further condensing product (B) in mole to mole ratio with salicylaldehyde at 125 to 175°C for 2 to 5 hours. The compounds function as anti-screen clogging and sediment stabilising additive agents for petroleum hydrocarbon distillate fuel oils and, as antioxidants and metal deactivators in both fuel oils and gasolines. Other publications, eg US-A-4,698,169 and EP-A-191967 disclose a reaction product useful as either a fuel or lubricant additive which is obtained by the reaction of an alkenyl succinic anhydride or acid with an aromatic secondary amine to form an intermediate product and thereafter reacting the intermediate product with either an alkanolamine, an aminomethane or a hindered alcohol.

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We have now found that the hydrocarbyl-substituted succinic diamides obtainable as described hereinafter are particularly useful as dispersants in fuel compositions.

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Accordingly in one aspect the present invention provides a hydrocarbon fuel composition comprising a hydrocarbon fuel and an amount sufficient to provide dispersancy of a hydrocarbyl-substituted succinic diamide, wherein the hydrocarbyl substituent is of a size sufficient to render the diamide soluble in the fuel, the diamide being obtainable by reacting at elevated temperature a secondary amine with either a hydrocarbyl-substituted succinic acid or an anhydride, ester or monoamide derivative thereof.

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The hydrocarbyl substituent of the succinic diamide is of a size sufficient to render the diamide soluble in the hydrocarbon fuel. Typically this may be achieved with a hydrocarbyl substituent having at least 25 carbon atoms, preferably greater than 35 carbon atoms, and up to about 500 carbon atoms, preferably up to about 300 carbon atoms. The hydrocarbyl substituent may be derived from a suitable polyalkene or mixture of polyalkenes selected from, for example, polyethylene, polypropylene and polybutenes. A preferred hydrocarbyl substituent is derived from a polyisobutene. Polyisobutene succinic anhydrides (PIBSAs) suitable for use in the reaction may be obtained commercially. They are generally prepared by reacting maleic anhydride with a polyisobutene by either a thermal or a chlorination route. An advantage of the thermal route for the preparation of PIBSAs is that it minimises contamination of the PIBSA with residual chlorine. Polyisobutene succinic acids suitable for use in the reaction may be obtained by hydrolysis of PIBSAs, suitably using water as the hydrolysing agent, and at elevated temperature. Polyisobutene succinic acid esters may suitably be obtained by esterification of either a PIBSA or a polyisobutene succinic acid. Polyisobutene succinic monoamides may suitably be obtained by reacting a PIBSA or a polyisobutene succinic acid salt with up to 1 mole per mole of a secondary amine.

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As the secondary amine there may be used a secondary mono-, di- or poly-amine. Thus there may be used a secondary mono-amine having the formula:-

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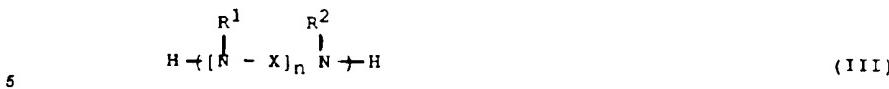
wherein R¹ and R² are independently C₁-C₁₅ hydrocarbyl groups, suitably alkyl groups, preferably C₁ to C₄ alkyl groups. Alternatively, there may be used a secondary diamine having the formula:-

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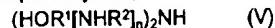
wherein X is a divalent hydrocarbyl group, suitably an alkylene group, having up to 15 carbon atoms, preferably up to 6 carbon atoms; and R¹ and R² are independently C₁ to C₁₅ hydrocarbyl groups, suitably alkyl groups, preferably C₁ to C₄ alkyl groups. Alternatively, there may be used a secondary polyamine having the formula:-



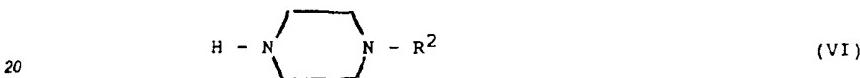
wherein X is a C₁ to C₁₅ divalent hydrocarbyl group, suitably a C₁ to C₆ alkylene group, preferably an ethylene or propylene group, which may be substituted with, for example, hydroxyl groups; R¹ and R² are independently C₁ to C₁₅ hydrocarbyl groups, suitably alkyl groups, preferably C₁ to C₄ alkyl groups; and n is an integer in the range from 1 to 6, preferably from 1 to 4. Preferred secondary amines include dialkanolamines of the formula:-



wherein R¹ = C₁ to C₆ alkylene, for example ethylene; derivatives thereof having the formula:-



15 wherein R¹ and R² are independently C₁ to C₆ alkylene, for example ethylene, and n is an integer in the range from 1 to 6, for example 1; and N-alkyl piperazines of the formula:-

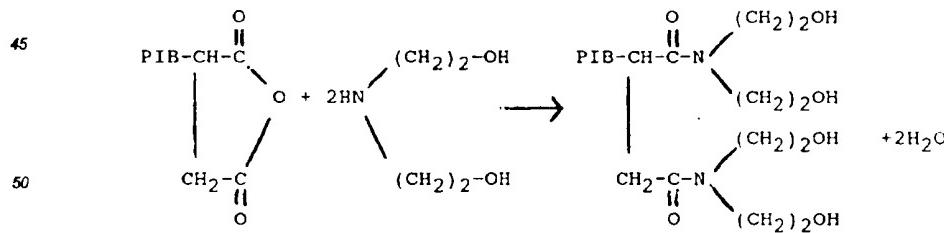


wherein R² is an alkyl group, suitably a C₁ to C₁₀ alkyl group, for example methyl, ethyl, propyl or butyl. Of these, N-alkyl piperazines are preferred because they eliminate the possibility of the diamide product being contaminated with esters, unlike compounds of the formulae (IV) and (V). A preferred secondary amine reactant is N-methyl piperazine.

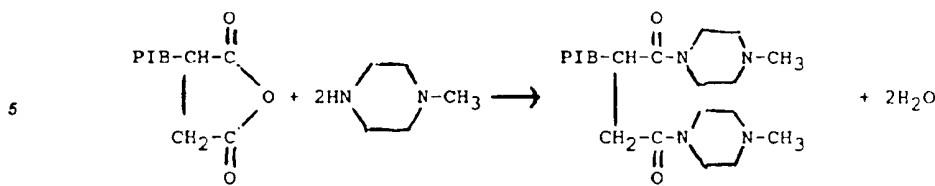
The hydrocarbyl-substituted succinic diamide is obtainable by reacting at elevated temperature a hydrocarbyl-substituted succinic acid or an anhydride, ester or monoamide derivative thereof with a secondary amine. The reactants are reacted in proportions such that there is formed a diamide. Using a hydrocarbyl-substituted succinic acid or anhydride it is preferred to react at least 2 moles of the secondary amine for each mole of acid or anhydride. Using a hydrocarbyl-substituted succinic acid monoamide it is preferred to react at least 1 mole of the secondary amine for each mole of monoamide. It is preferred to react a hydrocarbyl substituted succinic acid or anhydride with at least 2 moles of the secondary amine for each mole of acid or anhydride. Using a hydrocarbyl-substituted succinic acid monoamide as the starting material for the reaction with the secondary amine it is possible to produce diamides having different amido substituents by employing a secondary amine different to that used in the formation of the monoamide. Otherwise mixtures of diamides may be obtainable by using mixtures of at least two secondary amines in the diamide forming reaction.

The reaction may be accomplished in the presence or absence of a solvent. Suitable solvents include liquid hydrocarbons, for example xylene or cyclohexane.

40 The reaction of the acid or derivative thereof with the secondary amine may suitably be effected at elevated temperatures, suitably below 250°C, for example from about 90 to 180°C. The reaction of a PIBSA with diethanolamine, for example, may suitably be represented as follows:-



55 The reaction of a polyisobutene succinic acid with N-methyl piperazine, for example, may suitably be represented as follows:



10 The hydrocarbon fuel may suitably comprise a hydrocarbon fraction boiling in the gasoline range or a hydrocarbon fraction boiling in the diesel range. Gasolines suitable for use in spark ignition engines, eg automobile engines, generally boil in the range from 30 to 230°C. Such gasolines may comprise mixtures of saturated, olefinic and aromatic hydrocarbons. They may be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons. The octane number of the base fuel is not critical and will generally be above 65. In the gasoline, hydrocarbons may be replaced in part by alcohols, ethers, ketones or esters, typically in an amount up to 20% by weight. Alternatively, as the liquid hydrocarbon fuel there may be used any fuel suitable for operating spark compression engines, such as those which may be found in road vehicles, ships and the like. Generally, such a diesel fuel will boil in the range from about 140°C to about 400°C (at atmospheric pressure), particularly in the range from about 150 to 390°C, especially from about 175 to 370°C. Such fuels may be obtained directly from crude oil (straight-run) or from a catalytically or thermally cracked product or a hydrotreated product, or from a mixture of the aforesaid. Alternatively there may be used a biofuel, for example rape seed methyl ester. The cetane number will typically be in the range from 25 to 60.

20 The fuel composition contains the hydrocarbyl substituted succinic diamide in an amount sufficient to provide dispersancy. Typically in a gasoline fuel this amount will be in the range from 20 to 1000 ppm w/w based on the total weight of the composition. Typically in a diesel fuel this amount will be in the range from 10 to 500 ppm w/w based on the total weight of the composition.

25 The fuel composition may suitably be prepared by blending a concentrate comprising a fuel compatible hydrocarbon solvent and the hydrocarbyl-substituted succinic diamide with the hydrocarbon fuel.

30 The fuel composition in addition to the hydrocarbyl-substituted succinic diamide may contain known additives. The nature of the additives will depend to some extent on the end-use of the fuel composition. Diesel fuel compositions may contain nitrates or nitrites as a cetane improver, or copolymers of ethylene and/or vinyl esters, eg vinylacetate, as a pour point depressant. Gasoline fuel compositions may contain a lead compound as an anti-knock additive and/or an antioxidant, eg 2,6-di-tert-butyl phenol, and/or an anti-knock compound other than a lead compound, and/or an additional dispersant, for example a PIB polyamine. The other additives (if any) may be blended directly into the fuel composition or may be incorporated by way of a concentrate composition.

35 The invention will now be further illustrated by reference to the following examples.

40 EXAMPLE A

Preparation of "Clean" polyisobutylene succinic anhydride (PIBSA) for subsequent diamide preparations

45 A blend of 2 kg PIBSA (produced by the thermal maleinisation of a polyisobutene (PIB) of number average molecular weight (M_n) of about 1000) and 500 g of n-heptane was prepared. This was heated to about 80°C and then filtered through a diatomaceous earth filter aid. The filtration temperature was maintained at 50-60°C by the use of heat lamps.

50 The n-heptane was subsequently removed on a rotary evaporator at 110°C/28 inches Hg over one hour.

Some maleic anhydride (MA) was removed on the strip stage as evidenced by the condenser coils "furring up" with crystals.

Data from the determination of the residual MA and PIBSA No. (mg KOH/equivalent/g) of the various PIB-SAs is given in the following Table 1.

TABLE 1

| PIBSA | MA(%) | PIBSA No. |
|--|----------------|-----------|
| PIBSA | 0.3 | 103 |
| PIBSA 80/20 with n-heptane | 0.1 | 84 |
| PIBSA, diluted, filtered and stripped ie "clean" | less than 0.05 | 101.5 |

10

Example 1Preparation of Diamide

15 N-methyl piperazine (NMP)(25 g), the "clean" PIBSA of Example A (200 g) and xylene (100 g) were mixed and the mixture heated to reflux at 165-170°C. The mixture was held at the reflux temperature for 3 hours.

Water Evolution

20 Up to 3 hours - about 1.0 ml.
End of reaction - about 1.2 ml.

Solvent Removal

25 Charged - 312.7 g.
Product wt. - 207.9 g.
The product was stripped on a rotary evaporator at 130°C/29.5 inches Hg.

Analysis of Product

30 Total nitrogen - 2.8%.
Basic nitrogen - 1.6%.
Alkalinity value - 65.3 mg KOH/g.

Example 2Preparation of diamide

35 The "clean" PIBSA of Example A (200 g), xylene (100 g) and water (3.3 g) were mixed and heated to 90°C.
40 After one hour N-methyl piperazine (NMP) (25 g) was added and the mixture heated to reflux at 165-170°C, peaking at 173°C after 4½ hours.

Water Removal

| Time Elapsed | Water Removed |
|--------------------|---------------|
| 80 minutes (173°C) | 4.0 ml |
| 360 minutes (end) | 5.6 ml |

50

Solvent Strip

55 Charge - 304 g.
Product wt - 219.1 g.
The product was stripped on a rotary evaporator at 130°C/28 inches Hg.

Analysis of Product

5 Total nitrogen - 2.8%
 Basic nitrogen - 1.6%
 Alkalinity value - 62.7 mg KOH/g

Example 3Preparation of diamide

10 Example 2 was repeated except that instead of using xylene (100 g) there was used cyclohexane (100 g). In this preparation vigorous reflux occurred initially. A temperature of 107°C was attained. After removal of 16.8 g cyclohexane a reflux temperature of 140°C was attained.

15 Water Removal

| | Time Elapsed | Water Removed |
|----|--------------------|---------------|
| 20 | 65 minutes (107°C) | 1.5 ml |
| | 345 minutes (end) | 4.6 ml |

Solvent Strip

25 Charge - 271.3 g.
 Product wt - 206.2 g.
 The product was stripped on a rotary evaporator at 130°C/28 inches Hg.

30 Analysis of Product

35 Total nitrogen - 2.7%
 Basic nitrogen - 1.7%
 Alkalinity value - 66.6 mg KOH/g

Example 4Preparation of diamide

40 A "clean" PIBSA derived from a commercially available more reactive, ie higher vinylidene content (about 60%) PIB of M_n about 1300 was obtained by blending the PIBSA (715 g) and n-heptane (185 g) followed by filtering through a diatomaceous earth filter aid and removing the n-heptane solvent by rotary evaporation at 130°C/28 inches Hg (425 g blend charged; 400.1 g product recovered).

45 "Clean" PIBSA obtained as described above (202.9 g), xylene (100 g) and water (3.6 g) were mixed and held at 90°C for one hour to hydrolyse the PIBSA. N-methylpiperazine (NMP) (25 g) was then added and the mixture heated to 165-170°C at which point reflux commenced. A total of 4 hours reaction time was allowed before the product was stripped on the rotary evaporator at 130°C/28 inches Hg (charge 322.1 g; product wt. 220.1 g).

50 Analysis of Product

55 Total nitrogen - 2.3%.
 Basic nitrogen - 1.4%.
 Alkalinity value - 55.2 mg KOH/g.

Example 5Preparation of diamide

5 N-methylpiperazine (NMP) (60 g) (b.pt. 138°C) was added dropwise to a solution of commercially available PIBSA (75% solution derived from PIB of M_n about 1000 in an aromatic solvent) (400 g) in xylene (100 g) at 90-120°C over 15 minutes. An extra 100 g of xylene was added to stimulate reflux. Water (10 g) was added to hydrolyse the PIBSA. The temperature was then increased to reflux. Solvent was removed at 28 inches Hg/150°C.

10

Analysis of Product

15

| | Observed |
|------------------|----------|
| Total nitrogen | 2.2% |
| Basic nitrogen | 1.2% |
| Alkalinity value | 45.9 |

20

Example 6Preparation of diamide

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A mixture of a PIBSA identical to that used in Example 5 (400 g), xylene (230 g) and water (6.2 g) was charged to a one litre 5-necked flange pot reactor equipped with Eurotherm, agitator and Dean and Stark trap. The contents were then heated to 95°C to effect hydrolysis. Subsequently N-methyl piperazine (NMP) (64.8 g; b.pt. 138°C) was added.

30

The product was stripped at 150°C/28.5 inches Hg to remove solvents.

Analysis of product

35

| | |
|------------------|------------------|
| Total nitrogen | - 2.4%. |
| Basic nitrogen | - 1.5%. |
| Alkalinity value | - 59.5 mg KOH/g. |

Example 7

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Preparation of diamide

A mixture of a PIBSA identical to that used in Example 5 (400g), xylene (250g) and water (6.0g) was charged to a one litre 5-necked flange pot reactor equipped with Eurotherm, agitator and Dean and Stark trap. The contents were heated to 95°C and reacted for 2 hours prior to addition of N-methylpiperazinc (65.3g).

45

The product was stripped at 150°C/28.5 inches Hg.

Analysis of product

50

| | |
|------------------|-----------------|
| Total nitrogen | - 2.4%. |
| Basic nitrogen | - 1.3%. |
| Alkalinity value | - 51.2mg KOH/g. |

Example 8

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Engine testing of diamide product

Results were generated in an Opel Kadett engine test run on fuel treated with either 500 or 1000 ppm w/w of an additive package. The additive package was based on a commercial formulation modified in the respect

that the customary dispersant actives component was replaced on a weight/weight basis in turn by a dispersant according to the invention and prior art succinimide dispersants as indicated in Table 2 below. In Table 2 reference is made to succinimides 1 and 2. These materials are characterised as follows:-

Succinimide 1 is a mono-succinimide derived from an oil-free PIBSA identical to that used in Example 5, the amine used in the preparation being tetraethylenepentamine (TEPA).

Succinimide 2 is a bis-succinimide derived from an oil-free PIBSA identical to that used in Example 5, the amine used in the preparation being triethylenetetramine (TETA).

TABLE 2

| Disperant Used | Package Treat (ppm) w/w | Deposits mg/Valve | Manifold Rating | Valve Rating |
|----------------------------|-------------------------|-------------------|-----------------|--------------|
| Diamide (product of Ex. 7) | 500 | 13 | 7.88 | 9.90 |
| Diamide (product of Ex. 7) | 1000 | 6 | 8.95 | 10.0 |
| Succinimide 1 | 500 | 229 | 10.0 | 8.0 |
| Succinimide 2 | 1000 | 40 | 9.87 | 9.70 |

It can be seen from the results presented in Table 2 that the diamide product of the invention is superior in most respects to comparable succinimide dispersants in the Opel Kadett engine test.

Claims

1. A hydrocarbon fuel composition comprising a hydrocarbon fuel and an amount sufficient to provide dispersancy of a hydrocarbyl-substituted succinic diamide, wherein the hydrocarbyl substituent is of a size sufficient to render the diamide soluble in the fuel, the diamide being obtainable by reacting at elevated temperature a secondary amine with either a hydrocarbyl-substituted succinic acid or an anhydride, ester or monoamide derivative thereof.

2. A hydrocarbon fuel composition according to claim 1 wherein the hydrocarbyl substituent has from 35 to 300 carbon atoms.

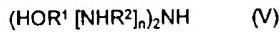
3. A hydrocarbon fuel composition according to either claim 1 or claim 2 wherein the hydrocarbyl substituent is derived from a polyisobutene.

4. A hydrocarbon fuel composition according to any one of the preceding claims wherein the secondary amine reacted with the hydrocarbyl-substituted succinic acid or derivative thereof is a dialkanolamine of the formula:-



wherein R¹ is a C₁ to C₆ alkylene group.

5. A hydrocarbon fuel composition according to any one of claims 1 to 3 wherein the secondary amine reacted with the hydrocarbyl-substituted succinic acid or derivative thereof is of the formula:-



wherein R¹ and R² are independently C₁ to C₆ alkylene groups and n is an integer in the range from 1 to 6.

6. A hydrocarbon fuel composition according to any one of claims 1 to 3 wherein the secondary amine reacted with the hydrocarbyl-substituted succinic acid or derivative thereof is an N-alkyl piperazine of the formula:



(VI)

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wherein R² is a C₁ to C₁₀ alkyl group.

7. A hydrocarbon fuel composition according to claim 6 wherein the N-alkyl piperazine is N-methyl piperazine.

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8. A hydrocarbon fuel composition according to any one of claims 1 to 7 wherein the hydrocarbyl-substituted succinic acid or derivative thereof is reacted with the secondary amine at a temperature in the range from 90 to 180°C.

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9. A hydrocarbon fuel composition according to any one of the preceding claims wherein the hydrocarbon fuel comprises a hydrocarbon fraction boiling in the gasoline range.

10. A hydrocarbon fuel composition according to any one of claims 1 to 9 wherein the hydrocarbon fuel comprises a hydrocarbon fraction boiling in the diesel range.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 1303

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int.Cl.S) | |
|--|--|--------------------|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.S) | |
| Y | US-A-4 234 435 (MEINHARDT ET AL.) * column 19, line 54 - line 58 * * column 21, line 9 - line 16 * * column 22, line 50 - line 53 * * column 23, line 5 - line 22 * * column 27, line 29 - line 65 * --- | 1-4,6, 8-10 | C10L1/22 | |
| Y | EP-A-0 062 161 (UNION CARBIDE) * page 8, line 15 - line 18; claim 1; example 1 * * page 19, line 8 - line 15 * --- | 1-3,6, 8-10 | | |
| Y | US-A-3 324 033 (KNAPP) * the whole document * --- | 1-4,8-10 | | |
| Y | DATABASE WPI Week 7637, Derwent Publications Ltd., London, GB; AN 76-69240X & JP-A-50 051 985 (TOA NENRYO KOGYO KK) * abstract * --- | 1-4,8-10 | TECHNICAL FIELDS SEARCHED (Int.Cl.S) | |
| D,Y | EP-A-0 191 967 (MOBIL OIL) * claim 1 * --- | 1-4,8-10 | C10L | |
| Y | GB-A-1 471 601 (TOA NENRYO KOGYO KK) * the whole document * --- | 1-4,6, 8-10 | | |
| A | GB-A-1 378 708 (BRITISH PETROLEUM) * the whole document * --- | 1-10 | | |
| A | EP-A-0 208 560 (EXXON) * the whole document * --- | 1-10 | | |
| | | -/- | | |
| The present search report has been drawn up for all claims | | | | |
| Place of search | Date of completion of the search | Examiner | | |
| THE HAGUE | 10 June 1994 | De La Morinerie, B | | |
| CATEGORY OF CITED DOCUMENTS | | | | |
| X : particularly relevant if taken alone | T : theory or principle underlying the invention | | | |
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| O : non-written disclosure | L : document cited for other reasons | | | |
| P : intermediate document | & : member of the same patent family, corresponding document | | | |



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Application Number
EP 94 30 1303

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int.Cl.) | | | | | | |
|--|---|--------------------|---|---|---|----------|-----------|--------------|--------------------|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | | | | | | | |
| A | FR-A-2 197 062 (ESSO) * claims 1-9 * | 1-10 ----- | | | | | | | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.5) | | | | | | |
| | | | | | | | | | |
| <p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>10 June 1994</td> <td>De La Morinerie, B</td> </tr> </table> | | | | Place of search | Date of completion of the search | Examiner | THE HAGUE | 10 June 1994 | De La Morinerie, B |
| Place of search | Date of completion of the search | Examiner | | | | | | | |
| THE HAGUE | 10 June 1994 | De La Morinerie, B | | | | | | | |
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